Synthesis and characterization of $LnAg(WO_4)(MoO_4)$

F. Fernández-Martínez , C. Colón , J.L. Montero , E. Atanes , C. Rivero

Universidad Politécnica de Madrid, E.U.I.T. Industrial, Ronda de Valencia 3, 28012 Madrid, Spain

Universidad Politécnica de Madrid, E.T.S.I. Telecomunicaciones, Avda. Complutense s/n, Ciudad Universitaria, 28040 Madrid, Spain

Abstract

Polycrystalline $LnAg(WO_4)(MoO_4)$ powders, with Ln = La to Lu and Y, have been obtained by ceramic method. Rietveld refinement for all compounds reveals that they present tetragonal symmetry, space group $I4_1/a$ (No. 88), where the Ln^{3+}/Ag^{+} ions are located in the $4a$ atomic positions, since the W/Mo are randomly distributed into $4b$ crystal sites.

In these compounds, a and b lattice parameters take values between those corresponding to tungstate and molybdate compounds. A progressive decrease in the lattice parameters is observed in going from La to Lu derivatives as a consequence of the well-known lanthanide contraction.

Keywords: Lanthanides; Tungstates; Molybdates; Optical properties

1. Introduction

The optical properties of lanthanide tungstates have been widely studied as host materials for laser designs. The strong anisotropy (leading to very large optical cross-sections) and large lanthanide impurity acceptance of the monoclinic [space group (SG) $C2/c$] $KY(WO_4)_2$ and $KGd(WO_4)_2$ single crystals with "ordered" cation environments have promoted their use as efficient laser hosts mainly for Nd^{3+} and Yb^{3+} ions. The double tungstate (DT) single crystals with tetragonal crystalline structure ("disordered" materials with regard to their actual cationic distribution) are also known as laser Raman shifters, and they received initial attention as laser crystals. These early laser experiments evidenced larger bandwidths and lower peak optical cross-sections than those observed in the ordered phases prepared. The interest on the tetragonal DT phases as lasants has been recently renewed after the achievement of $\Delta\lambda = 40$ nm of laser tunability range in a number of DTs doped with Yb

Recently we have prepared the monoclinic and tetragonal dimorphic phases of $AgNd(WO_4)_2$ In this study, the broad nature of the optical bands of Nd^{3+} in the tetragonal crystal was evidenced and its origin discussed. In the present work the tetragonal phases of $LnAg(WO_4)(MoO_4)$ polycrystalline powders have been prepared and their crystalline structures have been analysed.

2. Experimental

As starting materials Ag_2O, WO_3, $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ and rare earth oxides Ln_2O_3 (Ln = La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, Lu and Y), CeO_2, Pr_6O_{11} and Tb_4O_7 were used. $LnAg(WO_4)(MoO_4)$ polycrystalline powders were prepared by solid state reaction in air using stoichiometric amounts of the mentioned reactants which were heated at 700 °C in a ceramic crucible for 12 h. After cooling to room temperature, the samples were reground in an agate mortar and heated again at 750 °C for 12 h to complete the reaction, and then quenched to room temperature in air.

The crystal structure and purity of the samples were analysed by X-ray diffraction. The X-ray pattern was measured using Cu Kα radiation ($\lambda = 1.540598$ Å) with a Siemens D500 diffractometer equipped with a graphite monochromator. Data were collected at 300 K over an angular range of $5° \leq 2\theta \leq 118°$, scanning in steps of 0.05°, and a counting time of 10 s per step. The results were analyzed by the Rietveld profile refinement method, using FULLPROF program (December 2005 version)

3. Results and discussion

After identification of the scheelite phase for all the $LnAg(WO_4)(MoO_4)$ (Ln = La to Lu and Y) derivatives the Rietveld profile analysis for this polymorphic familly was performed in the tetragonal S.G. $I4_1/a$. The phase is well crystallized as it can be observed as an example in Fig. 1. The lattice parameters for these phases are given in Table 1, where the refinement

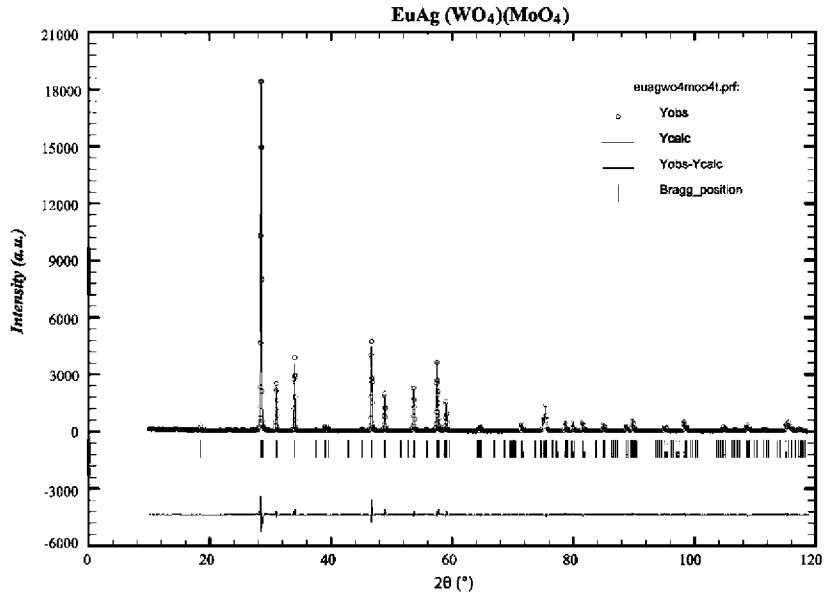

Fig. 1. Observed (open symbols) and calculated (straight line) X-ray powder diffraction pattern for $EuAg(WO_4)(MoO_4)$. R_p, 13.7; R_{wp}, 17.7; R_{exp}, 8.69; χ^2, 4.15. The short vertical lines below the patterns mark the positions of Bragg reflections. The bottom continuous line is the difference between the observed an the calculated intensity.

factors are also included. It can be observed a decrease in the lattice parameters with the increase in the atomic number of the rare earth according to the well-known lanthanide contraction that take place in going from La to Lu (Fig. 2).

The refinement was performed in the tetragonal S.G. $I4_1/a$ (No. 88) and the starting values for the unit cell and positional parameters were those reported for the $AgNd(WO_4)_2$ [7]. It has been found that the silver and lanthanide atoms randomly occupy the 2*a* site and also molybdate and tungstate are randomly distributed in the structure. The (1/2Ag + 1/2Ln), (1/2W + 1/2Mo) and O atoms occupy the 4*a* (1/2, 1/4, 3/8), 4*b* (0, 1/4, 5/8) and 16*f* (*x*, *y*, *z*) sites, respectively. The crystallographic positional parameters for $LnAg(WO_4)(MoO_4)$ after refinement are listed in Table 1.

A perspective view of the scheelite-type tetragonal structure is given in Fig. 3. It can be described as formed by chains along the a direction of alternate (Ln/AgO_8) bisdiphenoids and (WO_4/MoO_4) tetrahedra, which are sharing corners. Along the *c*-axis the (Ln/AgO_8) polyhedra of two consecutive chains are connected sharing one edge, forming dimmers of bisdisphenoids (Ln_2/Ag_2O_{14}). On the other hand, it can also be observed that all the tetrahedra are isolated one from another.

Its is worth noting that the $AgLnMoO_4WO_4$ derivatives for Ln = Ce, Pr and Tb have been obtained despite the relatively high instability of these trivalent ions. This behaviour could be explained from the redox properties of Ag_2O in the solid state reaction at high temperature, which stabilises the trivalent valence state.

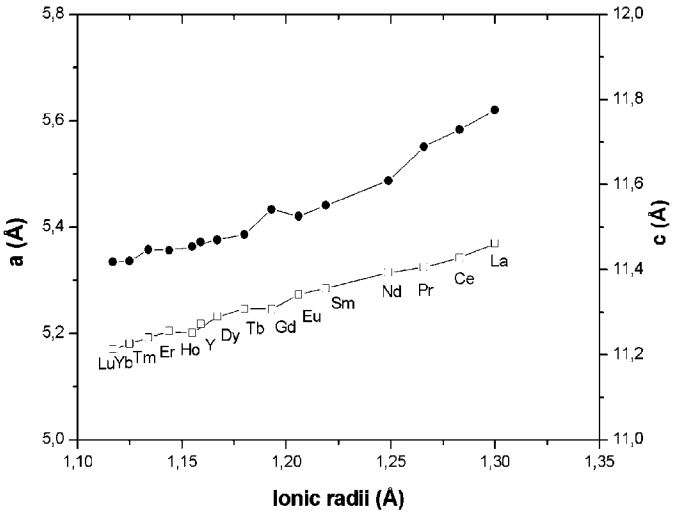

Fig. 2. Lattice parameters, *a* (squares) and *c* (circles), for $LnAg(WO_4)(MoO_4)$ vs. ionic radii of the rare earth.

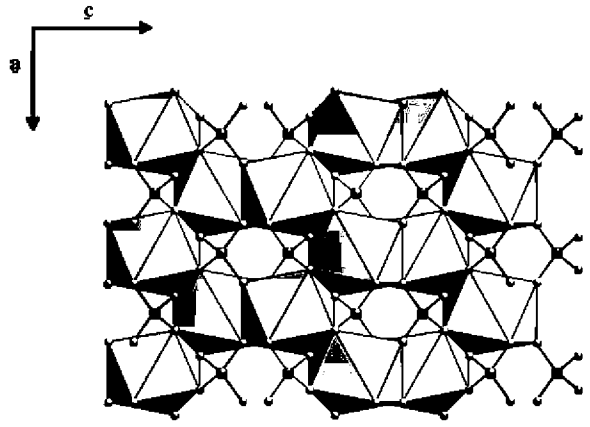

Fig. 3. Perspective view in the *ac*-plane of the scheelite structure showing the [Ag/LnO_8] bisdisphenoids polyhedra (closed face) and [W/MoO_4] tetrahedra (open face).

Table 1
Lattice parameters and crystallographic positional parameters for $LnAg(WO_4)(MoO_4)$

	a (Å)	c (Å)	V (Å^3)	O x	O y	O z	R_{Bragg}	R_F
La	5.3694(2)	11.7756(6)	339.49(3)	0.725(5)	0.612(5)	0.037(2)	9.81	15.3
Ce	5.3425(3)	11.7294(8)	334.78(3)	0.725(4)	0.610(4)	0.041(2)	7.07	9.79
Pr	5.3246(3)	11.6894(8)	331.41(3)	0.718(4)	0.613(4)	0.038(2)	8.18	13.7
Nd	5.3142(2)	11.6097(7)	327.87(3)	0.719(6)	0.602(5)	0.037(2)	7.12	8.50
Sm	5.2852(1)	11.5512(4)	322.66(2)	0.735(3)	0.603(2)	0.040(1)	4.73	7.13
Eu	5.2730(1)	11.5259(3)	320.47(1)	0.732(3)	0.601(2)	0.040(1)	4.55	6.08
Gd	5.2457(4)	11.542(1)	317.60(4)	0.726(4)	0.617(3)	0.045(2)	6.41	9.73
Tb	5.2463(1)	11.4831(4)	316.05(2)	0.732(3)	0.597(2)	0.040(1)	4.80	6.14
Dy	5.2312(2)	11.4702(5)	313.88(2)	0.733(3)	0.599(2)	0.042(1)	4.37	7.16
Ho	5.2009(6)	11.454(2)	309.81(7)	0.716(5)	0.608(5)	0.045(2)	10.3	10.7
Er	5.2044(3)	11.4453(9)	310.01(4)	0.733(5)	0.595(4)	0.041(2)	6.91	10.3
Tm	5.1919(6)	11.447(2)	308.58(6)	0.742(8)	0.594(6)	0.047(3)	14.0	13.7
Yb	5.1805(6)	11.420(2)	306.49(7)	0.731(8)	0.589(7)	0.048(3)	14.5	15.3
Lu	5.1700(7)	11.418(2)	305.20(8)	0.729(9)	0.592(8)	0.050(3)	17.7	16.6
Y	5.2172(2)	11.4655(7)	312.08(3)	0.737(3)	0.597(3)	0.042(1)	6.17	6.83

We are currently studying the very interesting optical properties of this family of silver–lanthanide molybdate–tungstate whose synthesis and characterization has been done in this previous paper.

References

A.A. Demidovich, A.P. Shkadarevich, M.B. Danailov, P. Apai, T. Gasmi, V.P. Gribkovskii, A.N. Kuzmin, G.I. Ryabtsev, L.E. Batay, Appl. Phys. B 67 (1998) 11.

A. Mayor, N. Langford, T. Graf, D. Burns, A.I. Ferguson, Opt. Lett. 27 (2002) 1478.

M. Rico, J. Liu, U. Griebner, V. Petrov, M.D. Serrano, F. Esteban-Betegón, C. Cascales, C. Zaldo, Opt. Express 12 (2004) 5362.

J. Liu, J.M. Cano-Torres, C. Cascales, F. Esteban-Betegón, M.D. Serrano, V. Volkov, C. Zaldo, M. Rico, U. Griebner, V. Petrov, Phys. Status Solidi A 202 (2005) R29.

C. Colón, A. Alonso-Medina, F. Fernández, R. Saéz-Puche, V. Volkov, C. Cascales, C. Zaldo, Chem. Mater. 17 (2005) 6635.

J. Rodriguez-Carvajal, FULLPROF Program for Rietveld Refinement and Pattern Matching Analysis, Lab. León Brillouin, CEA-CNRS, Saclay, France, 2005.

C. Colón, A. Alonso-Medina, J. Montero, F. Fernández, C. Cascales, J. Chem. Phys. 119 (2004) 13007.